

# PATENT SPECIFICATION

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International Classification:—C23c. H01g.

## COMPLETE SPECIFICATION.

### Improvements in the Manufacture of Metallised Polytetrafluoroethylene and Products thereof.

We, BRITISH DIELECTRIC RESEARCH LIMITED, a British Company, of Norfolk House, Norfolk Street, London, W.C.2, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the metallisation of polytetrafluoroethylene (hereinafter referred to as "P.T.F.E.") and the principal object of the invention is to provide a method of obtaining a strongly adherent layer of metal on P.T.F.E. by a chemical deposition process.

Metals deposited directly on to the surface of P.T.F.E. from a solution of a salt of the metal by the conventional chemical deposition processes do not adhere to the P.T.F.E. surface. It has been proposed to render the surface of P.T.F.E. active towards organic adhesive coatings by treatment with a fluid form of an alkali or alkaline earth metal, manganese or zinc to a controlled extent but we have found that, in general, such treatment does not enable strongly adherent chemically deposited metal layers to be obtained. The present invention is based on the discovery that when a particular form of this fluid treatment is used in conjunction with a particular type of chemical deposition process, strongly adherent layers of metal can be obtained on the P.T.F.E. surface. The fluid treatment is that comprising the use of a solution of sodium in ammonia and the deposition process used is that known as the "electroless nickel" process.

In accordance with the invention, adherent layers of nickel (containing nickel

phosphide) are obtained on the surface of P.T.F.E. by first treating the P.T.F.E. surface with a solution of sodium in liquid ammonia and then depositing a layer of nickel (containing nickel phosphide) on the pretreated surface from a solution of a nickel salt and sodium hypophosphite. Best results are obtained by using a pretreatment solution of from 0.1% to 5.0% by weight of sodium in liquid ammonia.

A single layer of nickel/nickel phosphide deposited on the P.T.F.E. surface by the chemical deposition process may itself act as an electrically conductive layer or serve some other purpose or alternatively it may form an anchor coat for a further layer of the same or a different metal or of a non-metallic material. A secondary metallic layer may be deposited on the nickel/nickel phosphide layer either by a chemical deposition method or by another method, e.g. by electrolysis or by evaporation in a vacuum. The material of the secondary layer, whether it is metallic or non-metallic, must be one which adheres to the primary metallic layer and one which does not attack either the anchor layer of the P.T.F.E.

The invention also comprises the utilisation of a metallised sheet or foil of P.T.F.E., prepared by the process described above, as the principal element of an electrical capacitor. Such an element may be made by depositing adherent layers of nickel/nickel phosphide on each side of a thin disc of sintered P.T.F.E. It can also be made, and generally more advantageously, by coating with nickel/nickel phosphide, both sides of a foil of P.T.F.E. which is coiled up to give a relatively large capacitance in a small volume of two such foils may be wound

[Price: ]

up together. A further possibility is to metallise one side of the foil only and to assemble two such metallised foils in a suitable manner to form the capacitor.

- 5 Such capacitors have peculiar advantages for certain conditions, particularly those where the great chemical and physical stability of P.T.F.E. can be utilised. One of the special ranges of operation is at comparatively high temperatures, since P.T.F.E. in the form of foil can be used without risk of instability up to 200° C. (and in other forms to a substantially higher temperature), and the nickel/nickel phosphide layer shows no tendency to oxidise at such temperatures.

Prior to the treatment with the solution of sodium in liquid ammonia, it is generally necessary to degrease the surface of the P.T.F.E., for example by immersion in acetone.

The following is an example of a method, in accordance with the invention, of depositing nickel/nickel phosphide on the surface of a P.T.F.E. foil.

When a 1% solution of sodium in liquid ammonia was used to treat the P.T.F.E. surface an immersion time in the sodium/ammonia solution of 1 to 5 seconds was satisfactory. After immersion in the sodium/ammonia solution the P.T.F.E. surface was washed with water.

The treated P.T.F.E. was sensitised by immersion for 1 to 2 minutes in a hot solution containing:—

Palladium chloride	0.1 g.
Concentrated hydrochloric acid	20 ml.
Water	80 ml.

It was then washed with a 0.6% solution of sodium hypophosphite and treated for 1 min. at 95° C. in a chemical nickel plating bath containing:—

Sodium citrate	60 g.
Ammonium sulphate	40 g.
Nickel sulphate	25 g.
Sodium hypophosphite	6 g.
Ammonia solution, sufficient to adjust pH to 8—9, preferably 8.5—9.0	
Water	to 1 litre.

After rinsing and drying, the P.T.F.E. carried a nickel/nickel phosphide coating of resistance 2—4 ohms/sq., and showing sufficient adhesion to enable soldered connections to be made to it.

Although we prefer to use an alkaline bath, it is possible to use an acid chemical nickel plating bath, for example one of the following composition:—

Nickel chloride	30 g.	60
Sodium hypophosphite	10 g.	
Sodium citrate	10 g.	
Water	to 1 litre	
Hydrochloric acid or Caustic soda sufficient to adjust the pH to 4—6.		65

Plating is carried out in this bath at 95°—98° C.

When a P.T.F.E. foil metallised by the process of the invention is to be used as an element in a capacitor, parts of the metal deposit (e.g. marginal strips) can be removed by solution in an acid, for example 6 N nitric acid.

It is more difficult to obtain a uniform coating of nickel/nickel phosphide on the P.T.F.E. surface than on other non-metallic surfaces and on metallic surfaces and we have found that in order to obtain a uniform coating it is necessary to take care to maintain the activity of the chemical plating bath. To this end it is preferable to use an alkaline bath maintained at a pH of between 8.5 and 9.0.

It is possible to obtain deposits of silver on P.T.F.E. surfaces by a chemical silvering process after pretreatment with the sodium/ammonia solution but the silver layers obtained in this way do not adhere strongly. In particular, when P.T.F.E. foils so metallised with silver are passed through the normal processes associated with the manufacture of wound electrical capacitors, the silver layer tends to flake or peel off the P.T.F.E. surface, whereas the metallised nickel layer remains undamaged and firmly adherent after passing through the same processes.

#### WHAT WE CLAIM IS:—

1. A method of obtaining an adherent layer of nickel (containing nickel phosphide) on a surface of P.T.F.E. comprising treating the P.T.F.E. surface with a solution of sodium in liquid ammonia and depositing the nickel layer on the treated surface from a solution of a nickel salt, and sodium hypophosphite.

2. A method of obtaining an adherent layer of nickel (containing nickel phosphide) on a surface of P.T.F.E., comprising treating the P.T.F.E. surface with a solution of sodium in liquid ammonia containing from 0.1% to 0.5% by weight of sodium, and depositing the nickel layer on the treated surface from a solution of a nickel salt and sodium hypophosphite.

3. A method as claimed in Claim 1 or 2 in which the solution of a nickel salt and sodium hypophosphite is maintained at a pH of between 8.5 and 9.0.

4. A method of obtaining adherent layers of metal on a surface of P.T.F.E.

comprising treating the P.T.F.E. surface with a solution of sodium in liquid ammonia, depositing a primary layer of nickel (containing nickel phosphide) on the treated surface from a solution of a nickel salt and sodium hypophosphite and depositing on the primary layer a secondary layer of the same or a different metal which is adherent to the primary layer and which does not attack the primary layer or the P.T.F.E.

5 A method as claimed in Claim 4, in which the secondary layer is deposited by a chemical deposition process.

6 A method as claimed in Claim 4, in which the secondary layer is deposited by an electrolytic process.

7 A method as claimed in Claim 4, in which the secondary layer is deposited by evaporation in a vacuum

8 A method of obtaining an adherent layer of a non-metallic material on an article of P.T.F.E. comprising treating the surface of the P.T.F.E. with a solution of sodium in liquid ammonia, depositing a primary layer of nickel (containing nickel phosphide) on the treated surface from a solution of a nickel salt and sodium hypophosphite and depositing on the primary layer a secondary layer of a non-metallic material which adheres to the primary layer and which does not attack the primary layer or the P.T.F.E.

9 An electric capacitor having as the principal element or elements P.T.F.E. sheet or foil having an adherent layer of nickel (containing nickel phosphide) deposited on one or both sides by the method claimed in any of Claims 1—3.

10 An electric capacitor having as the

principal element or elements P.T.F.E. sheet or foil having a primary adherent layer of nickel (containing nickel phosphide) and a secondary adherent metallic layer deposited on one or both sides by the method claimed in any of Claims 4—7.

11 An electric capacitor having as the principal element or elements P.T.F.E. sheet or foil having a primary adherent layer of nickel (containing nickel phosphide) and a secondary adherent non-metallic layer deposited on one or both sides by the method claimed in Claim 8.

12 A wound electric capacitor built up from one or more foils of P.T.F.E. having one or both sides coated with an adherent layer of nickel (containing nickel phosphide) by the method claimed in any of Claims 1—3.

13 A wound electric capacitor built up from one or more foils of P.T.F.E. having one or both sides coated with a primary adherent layer of nickel (containing nickel phosphide) and a secondary adherent metallic layer deposited by the method claimed in any of Claims 4—7.

14 A wound electric capacitor built up from one or more foils of P.T.F.E. having one or both sides coated with a primary adherent layer of nickel (containing nickel phosphide) and a secondary adherent non-metallic layer deposited by the method claimed in Claim 8.

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#### PROVISIONAL SPECIFICATION.

#### Improvements in the Manufacture of Metallised Polytetrafluoroethylene and Products thereof.

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adhesive coatings by treatment with a fluid form of an alkali or alkaline earth metal, manganese or zinc to a controlled extent but we have found that, in general, such treatment does not increase the adhesion of chemically deposited metal layers. The present invention is based on the discovery that when a particular form of this fluid treatment is used in conjunction with a particular type of chemical deposition process, strongly adherent layers of metal can be obtained on the P.T.F.E. surface. The fluid treatment is that involving a solution of sodium in ammonia and the deposition process used is that known as the "electroless nickel" process.

In accordance with the invention, adherent layers of nickel (containing nickel

phosphide) are obtained on the surface of P.T.F.E. by first treating the P.T.F.E. surface with a solution of sodium in liquid ammonia and then depositing a layer of nickel (containing nickel phosphide) on the pretreated surface from a solution of a nickel salt and sodium hypophosphite. Best results are obtained by using a pretreatment solution of about 1% by weight of sodium in liquid ammonia.

A single layer of nickel/nickel phosphide deposited on the P.T.F.E. surface by the chemical deposition process may itself act as an electrically conductive layer or serve some other purpose or alternatively it may form an anchor coat for a further layer of the same or a different metal or of a non-metallic material. A secondary metallic layer may be deposited on the nickel/nickel phosphide layer either by a chemical deposition method or by another method, e.g. by electrolysis or by evaporation in a vacuum. The material of the secondary layer, whether it is metallic or non-metallic, must be one which adheres to the primary metallic layer and one which does not attack either the anchor layer or the P.T.F.E.

The invention also comprises the utilisation of a metallised sheet or film of P.T.F.E., prepared by the process described above, as the principal element of an electrical capacitor. Such an element may be made by depositing adherent layers of nickel/nickel phosphide on each side of a thin disc of sintered P.T.F.E. It can also be made, and generally more advantageously, by coating, with nickel/nickel phosphide, both sides of a strip of foil of P.T.F.E. which is coiled up to give a relatively large capacitance in a small volume or two such foils may be wound up together. A further possibility is to metallise one side of the foil only and to assemble two such metallised foils in a suitable manner to form the capacitor.

Such capacitors have peculiar advantages for certain conditions, particularly those where the great chemical and physical stability of P.T.F.E. can be utilised. One of the special ranges of operation is at comparatively high temperatures, since P.T.F.E. in the form of foil can be used without risk of instability up to 200° C. (and in other forms to a substantially higher temperature), and the nickel/nickel phosphide layer shows no tendency to oxidise at such temperatures.

Prior to the treatment with the solution of sodium in liquid ammonia, it is generally necessary to degrease the surface of the P.T.F.E., for example by immersion in acetone. When a 1% solution of sodium in liquid ammonia is used an immersion time in the sodium/ammonia solution of 1—5 seconds is satisfactory. After immersion in the sodium/ammonia solution the

P.T.F.E. is preferably washed with water.

The following is an example of a method of depositing nickel/nickel phosphide on the surface of P.T.F.E. which has been pretreated in this way.

The pretreated P.T.F.E. was sensitised by immersion for 1 to 2 minutes in a hot solution containing:—

Palladium chloride	0.1 g.	
Concentrated hydrochloric acid	20 ml.	75
Water	80 ml.	

It was then washed with a 0.6% solution of sodium hypophosphite and treated for 1 min. at 95° C. in a chemical nickel plating bath containing:—

Sodium citrate	60 g.	
Ammonium sulphate	40 g.	
Nickel sulphate	25 g.	
Sodium hypophosphite	6 g.	85
Ammonia solution sufficient to adjust pH to 8—9.		
Water	to 1 litre	

After rinsing and drying, the P.T.F.E. carried a nickel/nickel phosphide coating of resistance 2—4 ohms/sq. and showing sufficient adhesion to enable soldered connections to be made to it.

Alternatively it is possible to use an acid bath, for example a bath of the following composition:—

Nickel chloride	30 g.	
Sodium hypophosphite	10 g.	
Sodium citrate	10 g.	
Water	to 1 litre	
Hydrochloric acid or Caustic soda sufficient to adjust the pH to 4—6.		100

Plating is carried out in this bath at 95°—98° C.

When a P.T.F.E. foil metallised by the process of the invention is to be used as an element in a capacitor, parts of the metal deposit (e.g. marginal strips) can be removed by solution in an acid, for example 6 N nitric acid.

It is more difficult to obtain a uniform coating of nickel/nickel phosphide on the P.T.F.E. surface than on other non-metallic surfaces and on metallic surfaces and we have found that in order to obtain a uniform coating it is necessary to take care to maintain the activity of the chemical plating bath. To this end it is preferable to use an alkaline bath maintained at a pH of between 8.5 and 9.0.

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